

The drying of clay minerals and mixed clay minerals

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In natural plastic clays used on ceramic compositions, the presence of certain minerals is frequently observed in the mineralogical composition. In this study, the drying ability of five different clay minerals was examined. All experiments were conducted under steady-state drying conditions. The sorption isotherm of the samples was determined by measurement of the mass of water absorbed at a fixed temperature versus the relative partial water pressure. The shrinkage of pastes was measured under the same experimental conditions. From the experimental data the heat of water sorption was calculated using a model which comes from the interpretation of a sorption reaction. The specific behaviour of the five clay minerals studied was observed; this can explain the behaviour of common plastic clays during the drying process. In particular, some investigations were conducted on mixed minerals. The results should support the possibility of obtaining a correlation between the heat of water sorption of certain clay raw materials and their mineralogical composition.

1. Introduction

1.1. Raw materials

Natural clays are highly variable in mineral content. To obtain a better knowledge of the types of minerals involved, a large group of clays for ceramic compositions was analysed. This preliminary study reveals the presence of a limited number of minerals, clay and non-clay minerals, which are prevalent in crude compositions. In this study, work was restricted to the understanding of the behaviour of certain clay minerals individually, i.e. kaolinite, montmorillonite, smectite, illite and illite–smectite. Our purpose in this work was to determine the heat of water sorption and the corresponding drying shrinkage as a function of the water content, of the five clay minerals previously mentioned. It is well known that very pure clay minerals do not exist alone in the natural environment. Therefore, we chose to study the behaviour of clay raw materials containing as high as possible a percentage of one of the mineralogical phases. We were looking for the most representative mineralogical phase of those analysed in the natural clays. The amount of the main components of their mineralogical compositions are listed in Table I. The following six clays were chosen.

(i) Kaolinite-based clay; a medium-ordered one from the region of Provins, France. Its crystal structure presents a significant proportion of random defects, translations and rotations in the plane (1001).

(ii) Illite clay, “Staub”, a well-crystallized and pure clay. It comes from lenticular forms traversing sandstone in the Vosges mountains in France.

(iii) Smectite-based clay; an interstratified vermiculite–smectite (80% smectite), purchased from Rivers, Poland.

(iv) Illite–smectite; an interstratified clay which contains 30% of smectite layers and 70% of illite layers. It comes from Czechoslovakia.

(v) Montmorillonite-based clay; a Wyoming natural clay. In the smectite group, its structural formula is closed to that of montmorillonite.

A high-purity quartz sand, whose grain size was lower than 40 µm, was used for a complementary experiment.

1.2. The drying process

Samples made with clay raw materials alone or clay mixed with non-plastic raw materials are porous. In wet samples, the water is held in the material by capillary forces on pores and micropores, and by chemical or physical adsorption on surfaces. Because of the limitation of the drying process to a temperature of 100 °C, the structural water which is removed beyond 100 °C, is not concerned in this study.

The interaction between water and clay mineral surfaces can be outlined: kaolinite presents a simple surface for water sorption. The interlayer spacing of non-intercalated kaolinite is not affected by humidity variation. In a similar way, only the outer surface of illite mineral is accessible to water sorption. Minerals containing vermiculite, smectite and montmorillonite, have many common features in their interaction with water. They all contain a large proportion of

TABLE I Mineralogical composition of clays

Natural clay	Mineral (wt%)				
	Kaolinite	Illite	Vermiculite-smectite	Illite-smectite	Montmorillonite
Kaolinite	87				
Illite		74			
Smectite	3		85		
Illite-Smectite				83	
Montmorillonite					91.5

swelling interlayers in which water molecules can be arranged in a partly ordered structure around the interlayer cations. The interlayer spacing depends on the type of those cations, but also on the absolute amount of water sorbed. This phenomenon would arise to a much greater extent if cations were adsorbed on non-interlamellar surfaces. Swelling properties are particularly dependent on the nature of the mineral and its characteristics, and also on its particle size.

Drying from a high moisture content leads to volume shrinkage. Therefore, if the drying process is carried out too rapidly, cracks and deformations may appear in the samples [1, 2]. In addition to that phenomenon common to all clay minerals, the materials of the smectite group, present a particular behaviour [3] which proceeds in a step corresponding approximately to the successive intercalation of three sheets of water in the interlamellar space.

During the drying process, the evaporation rate is dependent on the raw materials, on the texture of the sample and on the chemical potential of water related to the temperature and the relative humidity of the surrounding atmosphere. The migration of liquid and vapour water towards the sample surface occurs by means of capillary flow and diffusion. At the interface between the liquid and the surrounding atmosphere, a non-static and diffuse boundary layer exists in the material. Therefore, the measurement of the energy needed during the removal of water can provide information on all the bonding and transport mechanisms. In this study, in order to quantify only the sorption phenomenon we tend to minimize the water flow from the interior to the external surface of the sample by using steady-state drying experiments [4, 5]. In those conditions the quantity of water trapped in the clay remains in equilibrium with the ambient air-water vapour mixture for a time of drying which was experimentally determined.

2. Experimental procedure

The experimental apparatus used is shown in Fig. 1. It is a convection dryer in which constant air composition and temperature ($\Delta T = \pm 0.1^\circ\text{C}$) can be maintained. The relative atmospheric humidity, H , is controlled by means of an electric boiler and an indoor condensing unit ($\Delta H\% = 1\%$). Inside the chamber, the weight and length evolutions of cylindrical samples (1 cm diameter, 2 cm length) are continuously recorded. Length and weight at 100°C in air after 4 h are the chosen references for calculations. The vari-

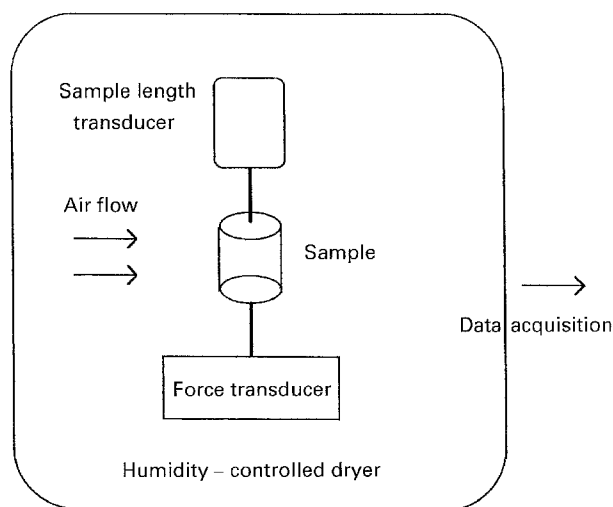


Figure 1 Experimental dryer equipped with weight loss and shrinkage transducers.

ation of the water content of a sample as a function of its length (drying plot), leads to information about the drying behaviour of bodies and shaped products, especially with respect to crack formation. The variation of the amount of water retained by clay as a function of temperature and relative partial pressure of water (sorption isotherm) can be analysed in terms of the clay surface and the free energy between clay and water.

As the total pressure, P_T , inside the dryer is constant, the heat of sorption, Q_t , is equal to the standard variation of enthalpy of the reaction H_2O (vapour) \rightarrow H_2O (sorbed). Therefore, it can be calculated using the integration form of the Clausius-Clapeyron equation

$$\ln(P_v)_t = \text{constant} + Q_t/RT \quad (1)$$

in which Q_t is considered to be temperature independent. If $(P_v)_t$ is the H_2O vapour partial pressure in equilibrium with a known amount of water sorbed per unit mass of clay, t , Q_t can be directly determined from the slope (Q_t/R) of the curve $\ln(P_v)_t = f(1/T)$.

Examples are presented in Fig. 2, for an illite-smectite clay, for four different percentages of sorbed water. As expected, the heat of sorption increases when the water content of the clay decreases. To obtain such results, over the whole range of sample humidity, we must overcome some difficulties due to the experimental uncertainties and to the variation in steps of Q_t for some clays. Therefore, it becomes necessary to perform experiments at several temperatures.

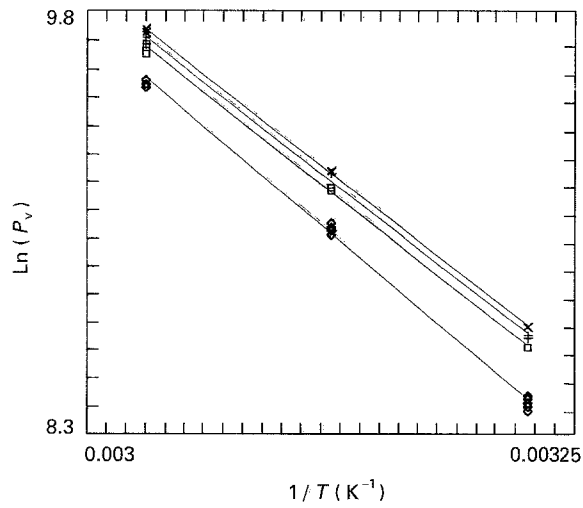


Figure 2 Partial pressure of water plotted against the inverse temperature for different sample humidities. The curves, from bottom to top, correspond to 5%, 20%, 30% and 40% humidity of samples.

The heat of water sorption can be approximated in a more simple way. The standard variation of the free energy of the reaction, free liquid water \rightarrow adsorbed water, is

$$\begin{aligned}\Delta G_t^\circ &= \Delta H_t^\circ - T \Delta S_t^\circ \\ &= \mu_{\text{H}_2\text{O}(\text{ads})}^\circ - \mu_{\text{H}_2\text{O}(\text{liq})}^\circ\end{aligned}\quad (2)$$

With $\mu_{\text{H}_2\text{O}(\text{liq})}^\circ = \mu_{\text{H}_2\text{O}(\text{g})}^\circ + RT \ln(P_{vs})$ and $\mu_{\text{H}_2\text{O}(\text{ads})}^\circ = \mu_{\text{H}_2\text{O}(\text{g})}^\circ + RT \ln(P_v)$ which leads to

$$\Delta G_t^\circ = RT \ln(P_v)_t / (P_{vs}) \quad (3)$$

where P_{vs} is the saturated partial pressure in equilibrium with free liquid water at a temperature, T . Combining Equations 2 and 3 we obtain

$$\ln(P_v)_t / (P_{vs}) = + \Delta H_t^\circ / RT - \Delta S_t^\circ / R \quad (4)$$

which is a linear function of $1/T$. The variation of enthalpy can be obtained from the corresponding slope. ΔS_t° was calculated as a function of sample humidity.

All the measurements were made at a constant temperature. When an equilibrium state was reached with a given partial pressure of water, P_v was reduced by a step of $1\% \text{ h}^{-1}$. In this way, heat transfer by convection favours a stable temperature and stable humidity fields in our small samples. Therefore, the heat of sorption can be calculated using the following equation

$$\begin{aligned}Q_t &= + RT (\ln \varepsilon + \Delta S_t^\circ / R) \\ &= \Delta H_v^\circ\end{aligned}\quad (5)$$

$\varepsilon = P_v / P_{vs}$ is the relative humidity of the air atmosphere and ΔH_v° the enthalpy variation of water desorption at T .

3. Results

The heat of sorption diagrams are presented in Fig. 3 for the five days minerals previously mentioned. The first stage of the behaviour is observed at high initial moisture content, corresponding to a weak increase of

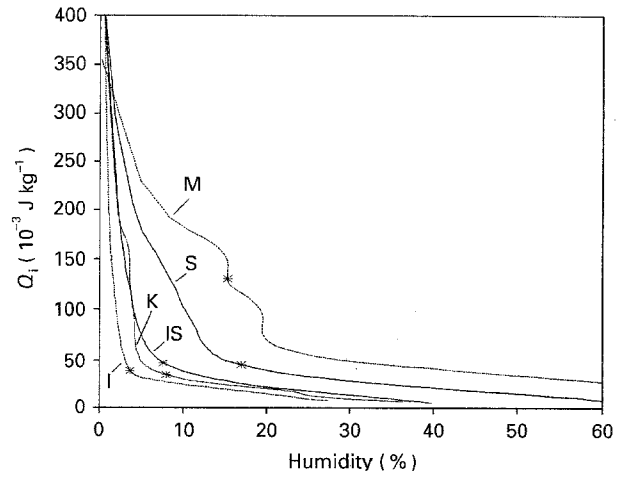


Figure 3 The heat of water sorption of different clay minerals as a function of the humidity of samples. M, Montmorillonite; S, smectite; K, kaolinite; IS, illite-smectite, I, illite. (*) The water content for a three-layer coverage.

the heat of sorption when the humidity ratio decreases. The situation is different for a lower water content; the heat of sorption becomes very sensitive to humidity. It is now well established that the first stage is associated with the removal of water from pores and from the external surface of particles [6]. During the second stage, the micropores are drained out and the main particular phenomenon is the desorption of water from the interlayer surfaces. Between the two stages, a transition exists which corresponds to the heterogeneity in the behaviour of the particles. The transition between the two stages can be determined using BET characterization. The BET equation is

$$x/x_m = c\varepsilon / [(1 - \varepsilon)(1 + (c - 1)\varepsilon)] \quad (6)$$

where x and x_m are, respectively, the mass of water sorbed per unit mass of clay, in the case of the experimental condition and in the case of a monolayer coverage. c is a parameter related to the heat of sorption. In a relative water pressure, ε , ranging from 0.07–0.35, a good fit of the BET equation was found with the experimental data. Over this range, no fitting attempts have been made because of the disturbance effect of phenomena such as pore filling. The BET theory leads to the determination of the weight of water required to cover the external and interlayer surfaces of particles, with a monomolecular layer [7–9]. Using an average cross-sectional area for a water molecule, it is possible to determine the specific surface (see Table II). Some calculations were made assuming that two or three layers of water molecules can fill the interlayer spacing. The calculated values, assuming that water content corresponds to three times the x_m parameter, are indicated in Fig. 3 by asterisk. These values are close to the beginning of the second stage of the curve. This result suggests that the low-humidity behaviour corresponds to the desorption of interlayer water, which can be predominant when micropores are drained out.

Some differences are noticeable among the five minerals. For kaolinite and illite, which are non-expanding clays, the second stage of the curve occurs at lower

TABLE II Specific surfaces

Kaolinite	174 m ² g ⁻¹
Illite	92 m ² g ⁻¹
Smectite	432 m ² g ⁻¹
Illite-Smectite	198 m ² g ⁻¹
Montmorillonite	388 m ² g ⁻¹

water contents. Illite-smectite clay presents a similar behaviour although it contains some expanding interlayers. This characteristic which differs from those of true smectite has been found elsewhere and is not yet well understood [10]. The smectite and the montmorillonite clays appear to contain more water in their expandable interlayer. This comes from their higher surface area and also from the characteristic of the interlayer surfaces and the type of cation sorbed. Two steps can be observed in the curves which are related to changes in the number of layers of water coverage [3]. The energy needed for the whole drying process can be evaluated from the surface between the humidity axis and each curve of Fig. 3. The values obtained are considerably higher for the smectite group than for the kaolinite, illite and illite-smectite group.

The drying curves of the five clay minerals are presented in Fig. 4. During the first stage, a quasi-linear evolution is observed for all the clays at the beginning of drying, i.e. at a higher water content. They move close together as water is removed. The corresponding shrinkage is high until the particles come into contact. After that the shrinkage rate decreases due to the formation of pores between particles in contact. For a lower water content, another type of behaviour is observed, corresponding to weight loss without any shrinkage. It is associated with water loss from the micropores and interlayer spacing. In Fig. 4, kaolinite and illite show a short pore-formation stage and a long last stage. In the case of swelling minerals, i.e. montmorillonite, smectite and interstratified illite-smectite, an additional shrinkage may be observed during the pore-formation stage. The last stage is then reduced to lower humidity values.

The behaviour of some mixed minerals was also studied. Two mixes of montmorillonite with quartz sand (mixes 1 and 2) were interesting because a variety of non-clay raw materials is often used as additives. Mixes of montmorillonite or smectite clays with kaolinite (mixes 3 and 4) are also of some interest. They are frequently used as natural mixes or resulting from the mix of variable raw materials. The compositions of the studied mixes are reported in Table III.

The drying curve for mix 2 is presented in Fig. 5. The quartz addition to montmorillonite clay leads to a more regular curve. The water loss from the micropores and interlayer spacing (last stage) occurs for a higher humidity content. The evolution with humidity of the heat sorption for montmorillonite clay and mixes 1 and 2 is presented in Fig. 6. Assuming that the quartz surface has a negligible role on the phenomenon of water sorption, we calculated the humidity values considering only the mass of clay. As expected, only a very small variation of the heat of sorption is observed for high water content when sand is added.

TABLE III Mineralogical composition of mixes

Mix 1: montmorillonite 0.75 + quartz 0.25
Mix 2: montmorillonite 0.50 + quartz 0.50
Mix 3: kaolinite 0.25 + montmorillonite 0.75
Mix 4: kaolinite 0.25 + smectite 0.75

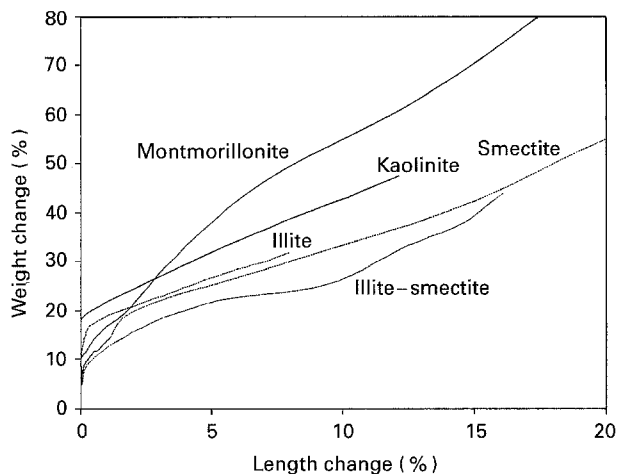


Figure 4 Weight loss plotted against shrinkage for the clay minerals.

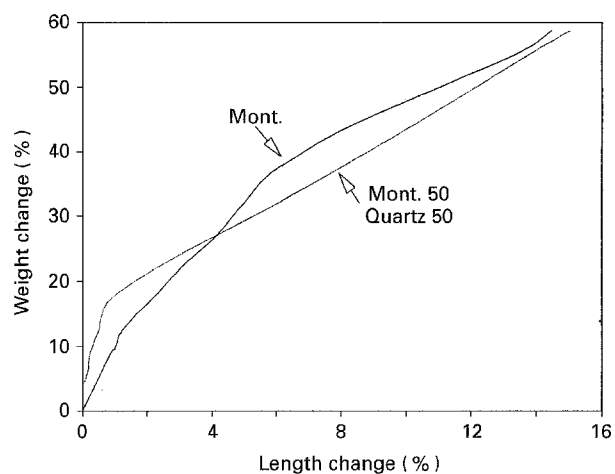


Figure 5 Weight loss plotted against shrinkage for montmorillonite and montmorillonite + quartz (mix 2).

However, at the lowest water content, the heat of sorption is larger than that determined for montmorillonite clay alone.

In Fig. 7, the evolution of the heat of sorption of mixes 3 and 4 compared with the minerals themselves is reported. For high water content, in both cases, the heat of sorption presents an intermediate value compared with those of the two minerals concerned. For lower humidity content, the heat of sorption of the mix is largely higher than those of the corresponding clay. In the higher water-content range, above 20% for mix 3 and above 8% for mix 4, a good fit is observed between the experimental results and calculated data interpolated from the individual values of heat of sorption of clay (Fig. 7).

From these results (Figs 5-7), a particular feature can be observed, for montmorillonite and to a lesser

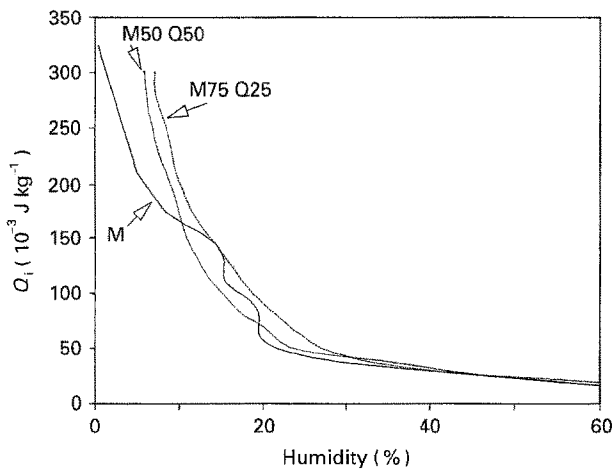


Figure 6 The heat of water sorption of montmorillonite, compared to those of montmorillonite + quartz (mixes 1 and 2), the humidity value being calculated in relation with the clay.

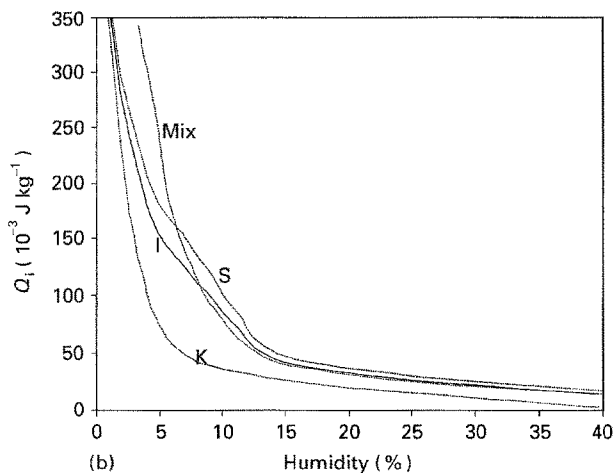
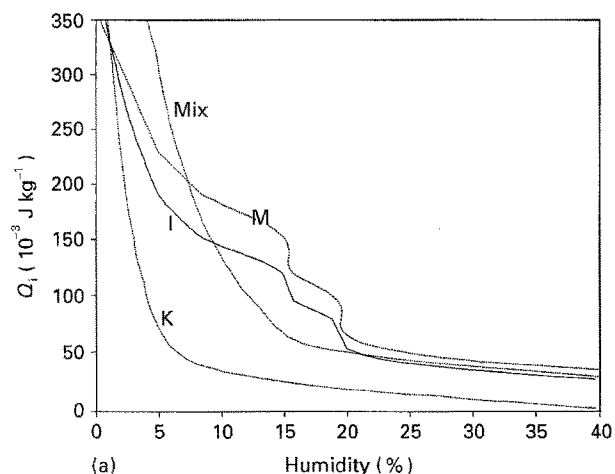


Figure 7 The heat of water sorption of (a) mix 3 and (b) mix 4. Clay mineral; (a) montmorillonite (M); (b) smectite (S), kaolinite curve (K), mix curve (Mix), interpolated curve (I).

extent for smectite. The swelling property disappears when kaolinite or sand is added. This result must be compared with that obtained with the illite-smectite clay which has no apparent swelling properties. A similar property was pointed out elsewhere [9] for a mixed layer mineral, montmorillonite-hydrous mica.

4. Discussion

For the three types of mixed minerals, the water concerned during the first stage of drying and at the beginning of the second stage is outside the packed particles. Under those conditions, when the drying is associated with shrinkage, the heat of sorption can be calculated from the mineralogical composition of the mix. The influence of sand addition on the water-loss phenomenon is confirmed (Fig. 6). It results from creating diffusion paths for water and vapour from the interior through sand and clay particle interfaces. For lower humidity content, beyond the beginning of the second drying stage, the experimental data diverge from the calculated data. In this drying stage the removal of water from the interlayer particles becomes the more important mechanism, therefore the phenomenon is mainly controlled by the nature of the clay. The reduction of shrinkage observed for mixes 1 and 2, during the last stage of drying can be due to a textural modification (Fig. 5). In a same way, for mixes 3 and 4 (Fig. 7), the discrepancy between experimental and calculated data may also be related to the past texture modification. The diffusion of water could be slowed by a more compact arrangement of particles of different size and shape.

The drying of similar porous and hygroscopic products has been described elsewhere [11], particularly from the kinetic point of view. A gradual evolution of moisture content is observed from the surface to the interior of the hygroscopic material. A similar situation must be assumed for our materials, although the long equilibrium time and the small sample size contribute to reduce the moisture gradient. The influence of water and vapour diffusivity through a material has to be considered. In particular, a capillary condensation phenomenon in micropores of a more or less compact product could influence the water departure. In this way, the heat of sorption values should represent not only the characteristic of the material but also a textural characterization to some extent.

In the case of mixed clay minerals the chemical influence of the interlayer-adsorbed species can modify the physical characteristics of clays [5]. For example, the occurrence of a cation exchange between clay minerals during the mixing process.

5. Conclusion

In this study we investigated the drying behaviour of the following clay minerals: kaolinite, montmorillonite, smectite, illite and illite-smectite. Their individual behaviour was compared to that of mixed minerals, i.e. montmorillonite or smectite with kaolinite or quartz sand. In this way, a better comprehension of the behaviour of mixed minerals is held, particularly when drying is associated with an important shrinkage. In that case it is possible to calculate the heat of sorption of the mixed minerals studied, from their mineralogical compositions. At the end of the last drying stage, some particular phenomena have an influence on the heat of sorption of the mixed material, whose values are much higher than those of the corresponding pure minerals. It could be the result of some textural or chemical effect.

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